

The class did very well on this exam. Congratulations.
Average score 81.2 with 1/3 > 85 and 2/3 > 77

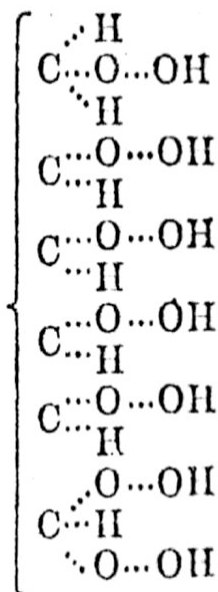
1. (6 min) **Identify** and **explain** at least **TWO FEATURES** of this diagram that were innovative at the time it was drawn, **AND ONE FEATURE** that came from a previous theory.

This formula for glucose from Couper's 1858 paper on the tetravalence and self-linking of the carbon atom uses triple dots to denote bonds from C to H or O and a vertical bracket to stand for the C-C bonds. Each of these features is of the greatest importance to his new idea about bonds.

A third innovation was to write C for carbon, rather than C₂, as he had done earlier in the paper. That is he decided to assign C an atomic weight of 12 rather than 6.

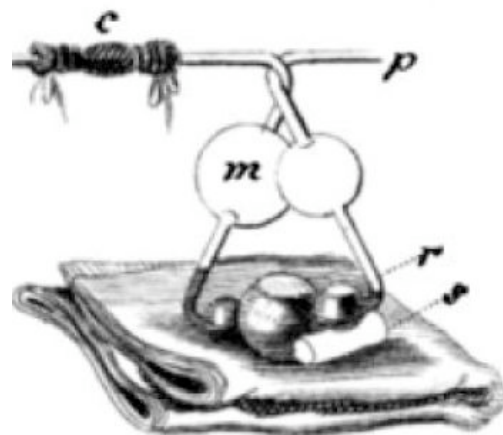
The idea of using the bracket to stand for all the vertical C-C bonds is a hold over from type theory. In fact in the French version of this paper he used vertical bonds instead of the bracket.

A somewhat less significant holdover is that he was still using O₂ for the oxygen atom (*i.e.* atomic weight 8, rather than 16).



2. (4 min) Explain **two clever features** in the design of this apparatus:

One design feature was to minimize the amount of glass to be weighted, so as to maximize the accuracy of measuring the difference from adding CO₂. This is achieved in two ways: first, the glass is very thin, necessitating the cloth cushion to keep it from breaking; second, the unlabelled bulb is smaller than bulb *m*, which needed to be big enough to hold most of the potash solution when upon cooling the combustion tube beyond *c* sucked the liquid back into *m*.



A second design feature was tilting the apparatus with cylinder *s*, so that the gases would bubble from bulb to bulb, stirring the solutions automatically and insuring complete absorption of CO₂.

There are a number of other features, like twisting the 5-bulb apparatus into a very compact form to facilitate handling and weighing it.

3. (7.5 min) When Prof. Wiberg drew this diagram, he was encoding lots of information or ideas. Explain how one or two aspects of the information, ideas, or notation would have been familiar to or invented by each of the chemists below. **Do not use the same information, idea, or notation twice**, but try to mention all of them.

Lavoisier (~1790)

Lavoisier classified and named the elements Hydrogen and Oxygen, and he measured the mass ratios of these elements in organic substances by combustion. These features are obviously present in the formula. [It is true that he focused on acidification by oxidation, but this compound is not acidic.]

Berzelius (~1830)

Berzelius invented the symbols for the elements that we use now, and the idea of writing numbers next to the symbols to denote atomic ratios. He also measured good atomic weights. Thus he was accustomed to writing formulas that expressed **Composition**. [If the grader wrote # on your paper, it is because you failed to comment on the atomic ratios.]

Pasteur (~1848)

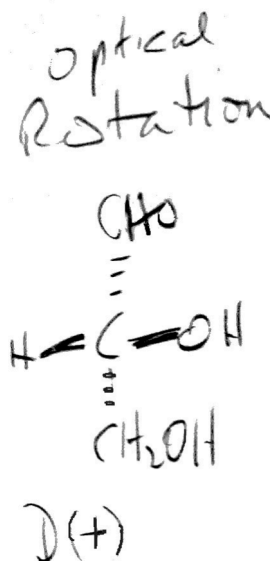
In organic chemistry Pasteur is most noted for measuring optical rotation after separating a racemate into enantiomers. Thus he would have been familiar with the idea of "optical rotation" and the idea the (+) might imply rotating polarized light to the right.

Crum-Brown (~1860)

Crum-Brown drew **Constitutional** formulae in which Berzelius's atomic symbols were connected by lines denoting bonds with double or triple lines to denote double or triple bonds. (Actually he had the symbols enclosed in circles, but this is a minor point.)

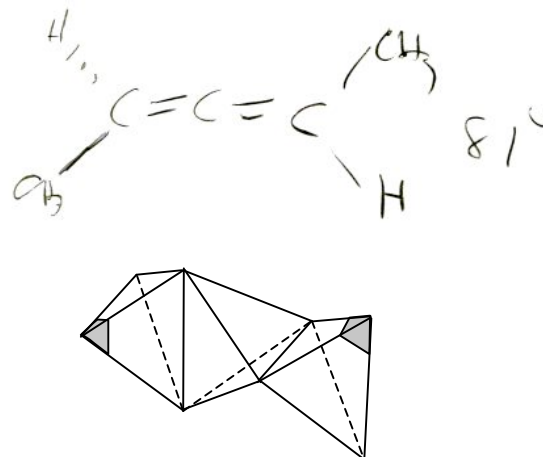
Fischer (~1890)

Fischer devised his Projection to denote **Configuration**. He had the idea of understanding horizontal substituents to be projecting from the page and having vertical bonds retreat into the page from stereogenic carbons. He also had the idea of using D and L to denote configuration relative to (+)-gluceraldehyde, according to chemical interconversions.



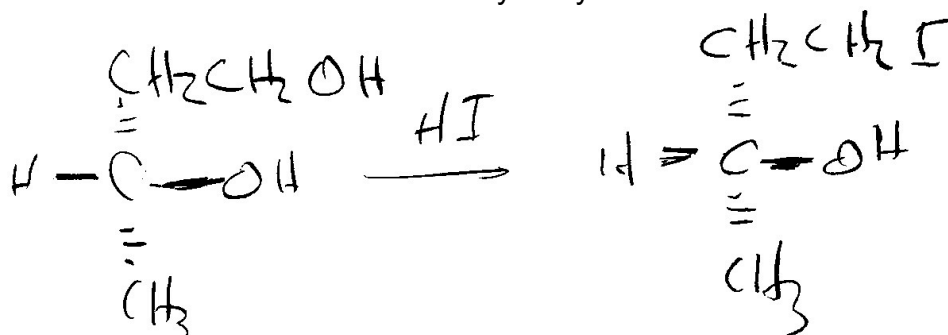
4. (4 min) When Prof. Wiberg drew this diagram, you should have thought of a long history involving stereochemical THEORY AND EXPERIMENT involving molecules with this functional group. Tell the story in a few sentences. It might help to draw a contemporary diagram.

In 1874 van't Hoff proposed that such disubstituted allenes should exist as enantiomer pairs, and he illustrated his suggestion with an illustration showing a tetrahedron sharing opposite edges with two others. His prediction was not confirmed by experiment until 1932, when Kohler and his collaborators resolved such allene enantiomers, thus proving their chirality.

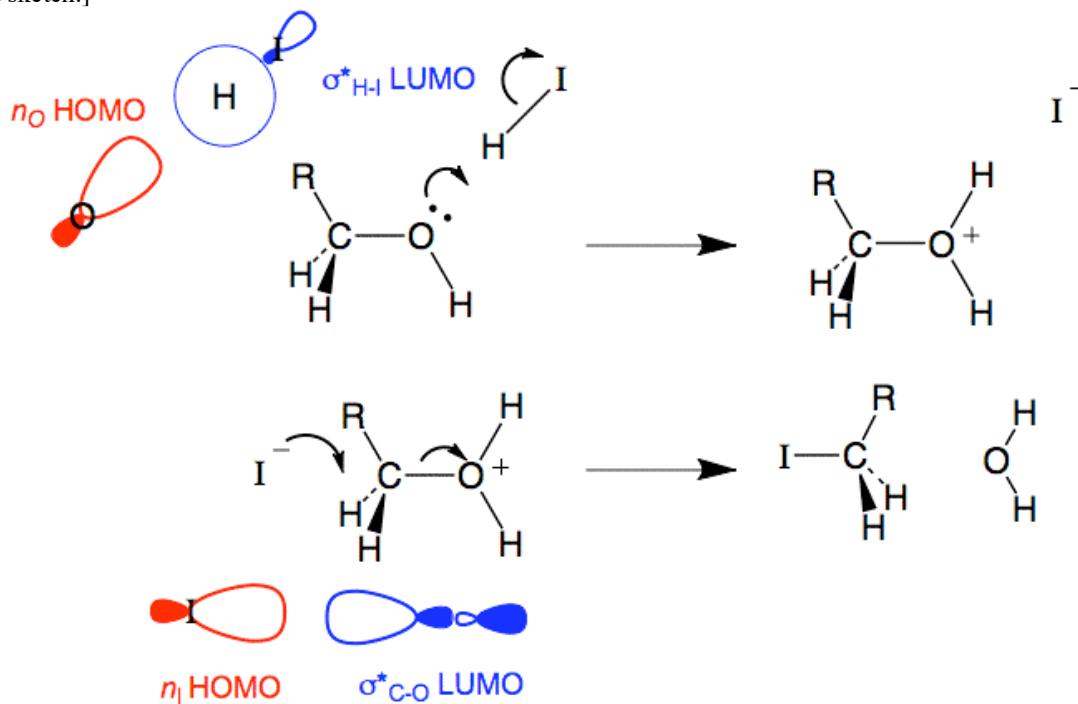


5. (2 min) Give the formal constitutional **Name** for the **Product** of the following reaction:

3-hydroxy-1-iodobutane or 4-iodo-2-butanol



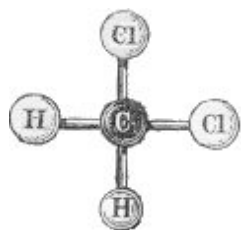
6. (5 min) Use **curved arrows** and relevant electron pairs to draw **the most straightforward two-step mechanism** for the transformation shown in Question 5. [You may simplify the structures you draw by using R to abbreviate whatever is not directly involved in the relevant localized HOMOs or LUMOs, which you should identify and sketch.]



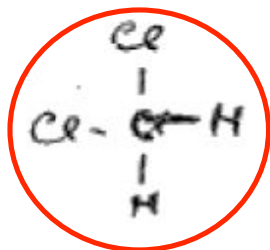
7. (3.5 min) Explain briefly how **isomorphism** played a role in the development of atomic theory.

The similarity in crystal shape between ammonium arsenates and phosphates showed that whatever role As played in the former P played exactly the same role in the latter. Thus the ratio of atomic weights of As and P was available from the ratios of their weights to those of the other constituents in these crystals. This was one solution to the puzzle of what we would now call the valence of atoms, which appeared then as uncertainty in the atom ratios of compounds with known weight ratios of the elements.

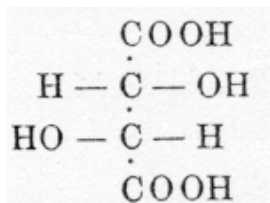
8. (6 min) Seemingly similar diagrams can mean very different things to different people. **IN TERMS OF WHAT THE AUTHOR INTENDED TO SHOW**, two of these diagrams (from 1865, 1869, and 1891) could be regarded as true to our current understanding of molecular structure, but one of them is now known to be wrong. **CIRCLE** the **WRONG** one, and **EXPLAIN** briefly what each of the three authors was trying to convey.



This croquet ball model was used by Hoffman in his 1865 lecture on **constitution**, in particular the tetravalence of carbon. He had no intention of showing arrangement of atoms in space, so what he was showing remains correct from our modern point of view.



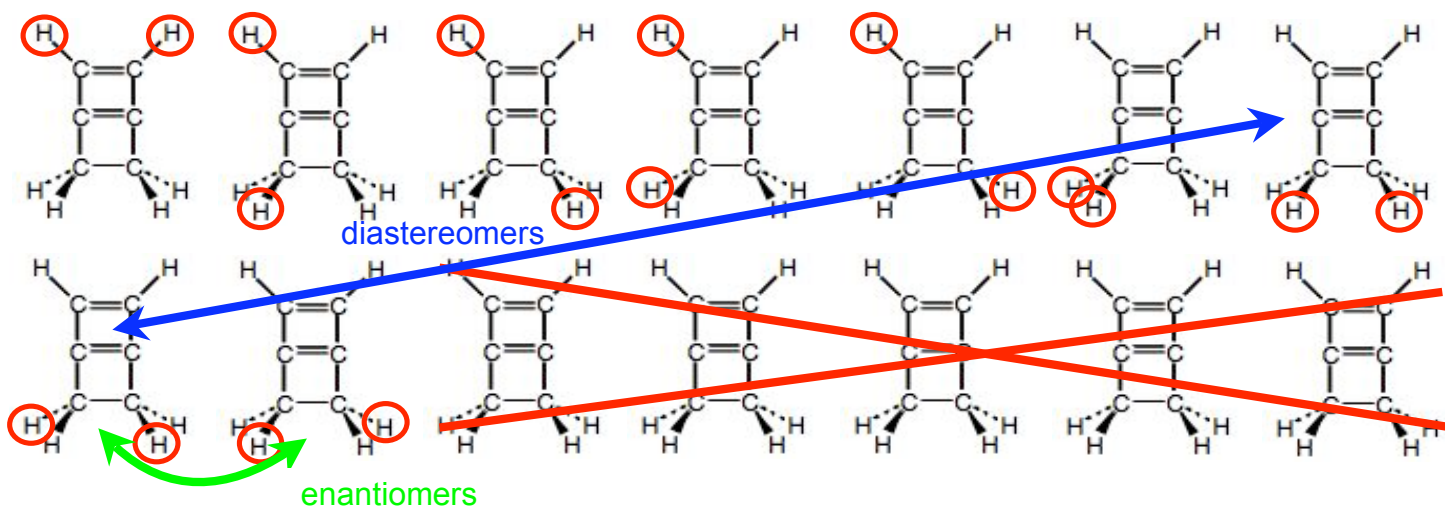
This incorrect structure was included in Lieben's 1869 cautionary letter to his former student Paternó, who had published an explanation of the supposed existence of three isomers of dibromoethane based on different arrangements in space of the atoms. Lieben warned that discussing arrangement of atoms in space using such a model for dichloromethane would predict two isomers, showing that he had completely missed the relevance of Paternó's proposal of a tetrahedral structure for carbon, which predicts only one isomer. "Shooting off into space in search of atoms one risks losing the ground under his feet" was his unimaginative advice.



This is Fischer's projection of tartaric acid. He meant only to show **configuration**, not to provide an accurate picture of actual atomic positions in 3D space. Such projections are still in use (for example in Prof. Wiberg's lecture).

9. (6 min) **CIRCLE** two H atoms on enough of the molecules below to show ALL "non-homomeric" isomers that are **DISUBSTITUTED** with two **IDENTICAL** groups. Connect **ONE** of your structures with **TWO** others so as to illustrate (and **NAME**) both kinds of stereochemical **RELATIONSHIP**. At the end cross out the structures you do not need.

(Note that configurational diastereomer pairs must include the top right molecule. Others differ in constitution.)



10. (6 minutes) Choose **either** the Unitary **or** the Dualistic theory of organic chemistry and explain the following:

a) What experiment(s) suggested the theory

Unitary: Substitution reactions showed that atoms could be replaced without changing a molecule's "type" (*e.g.* product from chlorination of acetic acid is still an acid). Inconsistent with radical theory because radical "elements" could be "transmuted" and with dualism because negative chlorine could substitute for positive hydrogen.

Dualistic: Electrolysis showed that compounds could be separated into positive and negative components (*e.g.* Davy's electrolysis of potash gave positive potassium). The concept of molecules' associating by positive-negative attraction was extended to organic chemistry when Liebig and Wöhler found that the benzoyl radical (C_7H_5O) persisted through numerous "double decompositions" in which its partner was changed.

b) Where the name of this theory means

Unitary: persistence of a wholistic unit "type" through chemical transformations. Contrast to dualism.

Dualism: Two kinds of charge. Opposites hold together.

c) On what basis Couper criticized this theory in 1858.

Unitary: The idea that one compound could be transformed to any other one by addition and substitution of atoms was too general to have any predictive power. Common sense said that this was silly, like saying that words could be transformed into others by adding, subtracting, or changing letters.

Dualism: In treating radicals as permanent, the dualistic theory ignored the most important question, namely what makes the atoms hold together to form radicals. Attention should be focused on the combining power of individual elements, not that of groups of atoms.

d) A way in which this theory influences how we discuss modern organic chemistry.

Unitary: IUPAC nomenclature is based on the idea of substitution with a fundamental alkane root name and prefixes for substituents combined to form a single unitary word, *e.g.* chloromethane.

Dualism: We still speak of groups of atoms as radicals and denote them as "R". One way we name organic compounds is as if they were formed by association of positive and negative radicals, separated by a space between the two words, *e.g.* methyl chloride.